

Interfacial phenomena in biocorrosion

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Abstract - In natural environments, microbes attach to engineering materials and colonize the surfaces to produce biofilms. Biofilms mediate the interactions between surfaces and environment resulting in serious energy losses, reduced equipment performance and corrosion failures in several defence and industrial systems. The chemical processing industry, oil and gas industry, power generation industry and the defence services have acknowledged the prevalence of biocorrosion in their operating systems. Microbial activity seemed to be involved in most of the cases of failure of the systems where mild steel, iron and copper alloys were used.

The present paper incorporates the data obtained in respect of three different corrosion behaviours of structural materials viz., an easily corrodable surface (mild steel), a corrosion resistant surface (304 stainless steel) and a complex corrosion behaviour (copper). Microbiological and electrochemical methods have been used to study the interfacial properties of metallic surfaces covered with biofilms. The biologically conditioned interfaces have been characterised by selecting suitable parameters in metal biofilm systems. The biofilm/passive layer interactions have been interpreted on the basis of charge transfer and diffusion controlled reactions taking into account adsorbed reaction intermediates or products.

In natural environments, microbes attach to engineering materials and colonize the surfaces to produce biofilms (ref. 1). The biofilm comprising of a variety of bacteria, their metabolites, water borne detritus and corrosion products, is bordered by two interfaces; the fluid and the substratum. The dissolved and particulate materials entrapped in the biofilm are constantly being transported across one or both of the interfaces (ref. 2). Microbial colonization can change the corrosion behaviour of metals by locally changing the type and concentrations of ions, pH and oxygen levels as well as by introducing diffusional barriers to the transport of chemical species at the metal solution interface (ref. 3). These varied effects result in changes in passive film composition, type of corrosion products, and electrochemical behaviour of metallic materials.

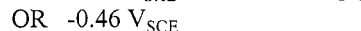
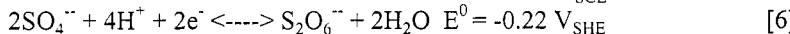
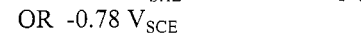
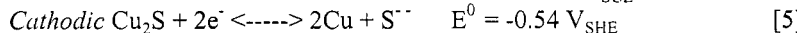
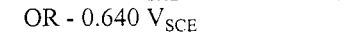
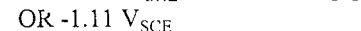
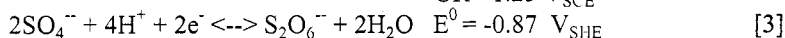
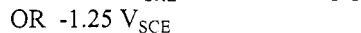
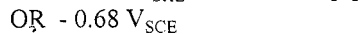
The present paper incorporates the observations made on the role of bacteria in promoting the localised corrosion to three different structural materials viz mild steel, copper and 304 stainless steel. An attempt has been made, to characterise the microbial biofilms processes modifying the protective effect of passive films. For

this, two sulphate reducing bacteria (SRB) viz., *Desulfovibrio desulphuricans* and *D. vulgaris*, and one aerobic species *Comamonas testosteronii* were identified at NCIMB, Aberdeen (UK) were used as test organisms. For the isolation, identification, stock culturing and purity checks of SRB, methods of Postgate (ref. 4) and for estimating H₂S production ASTM (ref. 5) were followed. The cyclic potentiodynamic anodic polarisation, and AC impedance measurements were carried out with test electrodes of mild steel, copper and AISI type 304 stainless steel exposed to cultures of bacteria as well as abiotic control using the experimental setup of Wilde (ref. 6) and De and co-workers (ref. 7) employing ASTM (ref. 8). Potentials were measured against a saturated calomel electrode (SCE) with an agar-agar/ KCl bridge. AC impedance data were obtained at frequencies ranging from 0.05 Hz to 20 kHz and a peak amplitude of 5 mV. The lowest frequency of 0.05 Hz was selected as there was a wide scatter in the results below that frequency.

The accelerated corrosion as a consequence of the presence of microorganisms particularly SRB have earlier been reported. The action of SRB is not limited to mild steel and has also been reported for copper and its alloys and stainless steels (refs. 9,10). Both the latter metals have a greater resistance to corrosion than mild steel and it is generally considered harder to induce corrosion in these metals particularly stainless steel (ref. 11). This is due to formation of a natural passive layer, which prevents the metal in reverting to the thermodynamically stable oxide (ref. 12). The exact nature, structure and composition of this passive layer is still not established. It is generally agreed that passivity is due to formation of a surface film which acts as barrier to further corrosion.

In the present study, mild steel, as an easily corrodable surface, exhibited a complex biofilm/inorganic layer interaction. Copper also showed a complex corrosion behaviour. Laboratory experiments have revealed that the two SRB species, *D. desulphuricans* and *D. vulgaris* are indeed responsible for severe pitting type of corrosion on these surfaces. It has been reported that corrosion increases with an increase in hydrogen sulphide and cathodic current density is directly proportional to log of hydrogen sulphide concentration (ref. 13).

As an immediate consequence of hydrogen sulphide formed, the metal ions present in the interfacial region of corroding metal undergo chemical reaction forming and depositing metal sulphides on the pores and in the defects of the surface films. The interfacial surface film in such a case comprises of mixed hydrated oxides and sulphides of the respective metals. The following electrochemical reactions are expected to occur on mild steel and copper exposed to seawater medium containing the two anaerobes (SRB).



E^0 represents standard reduction potential, *SHE* represents standard hydrogen potential and *SCE* represents saturated calomel electrode.

It is of interest to note that the measured values of corrosion or mixed potentials of both mild steel and copper closely correspond with the values calculated from the standard potential values of reactions [1] [2] and [3] for mild steel and reactions [4] and [5] for copper (ref. 14). The observed shifts in corrosion presumably arise as a result of the acceptance of electrons by the metal sulphides produced as a consequence of biogenic production of hydrogen sulphide.

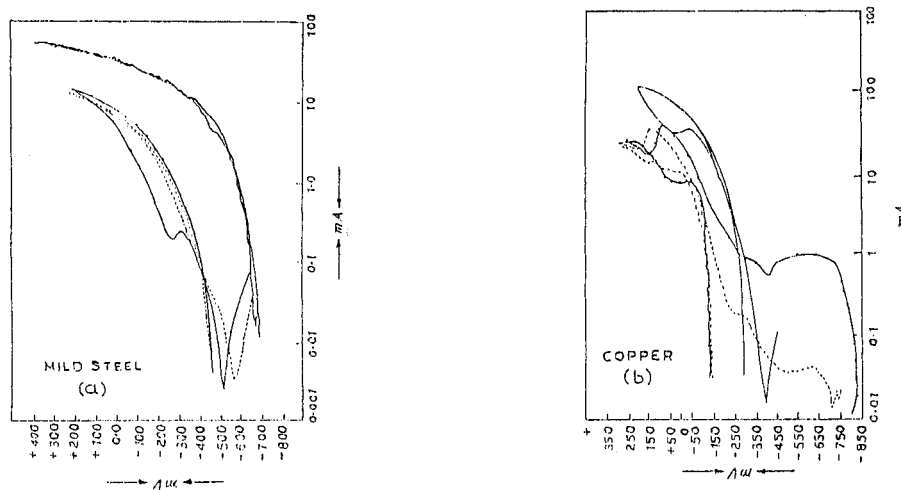


Fig. 1a,b :Potentiodynamic anodic polarisation curves of (a) mild steel and (b) copper in abiotic control; lactate seawater media (solid curves) ; medium containing *D. desulphuricans* (dashed curves); medium containing *D. vulgaris* (solid dotted curves).

The anodic polarisation curve for mild steel (Fig. 1a) showing an active behaviour in abiotic medium, displays a small passive potential region in the media containing each of the two species of bacteria. In the case of *D. vulgaris*, however, a distinct hysteresis loop is noted at reversal of potential scan. Wilde (ref. 6) has attributed the formation of such hysteresis loop to pitting corrosion reactions. Copper, on the other hand (Fig. 1b) while exhibiting an active behaviour in abiotic medium, displays a pronounced passive behaviour in the media containing anaerobes. This reflects the active passive behaviour of copper under the influence of SRB species. However, the current density for passivation in presence of *D. vulgaris* is considerably higher than that of *D. desulphuricans*. An enhanced passive behaviour of the former species, is therefore, evident. This passivity is of temporary nature and is attributed to mixed hydrated oxide and sulphide interface. On reversal of the potential scan, copper exhibits total irreversible behaviour indicating thereby total alteration in its interfacial film composition. The presence of sulphide corrosion products at the interface accelerates the anodic reactions [1] and [4] in mild steel and copper. These anodic regions eventually become nuclei for pitting corrosion.

In case of 304 stainless steel, a corrosion-resistant alloy; the biofilm/metal interactions has led to favourable corrosion conditions. This is evident from a loose uniform deposit of polymeric materials and pitting as well as crevice corrosion in presence of test bacteria (*C. testosteronii* and *D. vulgaris*). An accelerated localised attack mainly pitting corrosion is ensued by formation of differential aeration cells and through an alteration of oxygen gradients. The bacterial film in this case acts as a barrier for oxygen diffusion. As has been reported by several authors (ref. 3), the respiratory

activity of microbes within biofilm lead to modification of oxygen profile at the metal-solution interface. This results in an ennobling effect on the corrosion potential. The DC polarisation data suggest reduction in pitting potential ($200 \text{ mV}_{\text{SCE}}$) at zero hour (Fig. 2a) and also indicate that the presence of *C.testosteronii* in the coculture brought about changes in the environment within 24 hour that were conducive to pitting corrosion (Fig. 2b). This is evident from slopy plateau regions, higher passive current densities and lower pitting potentials as indicative of a crevice corrosion tendency. However, the pitting tendency was found more evident than the susceptibility to crevice corrosion.

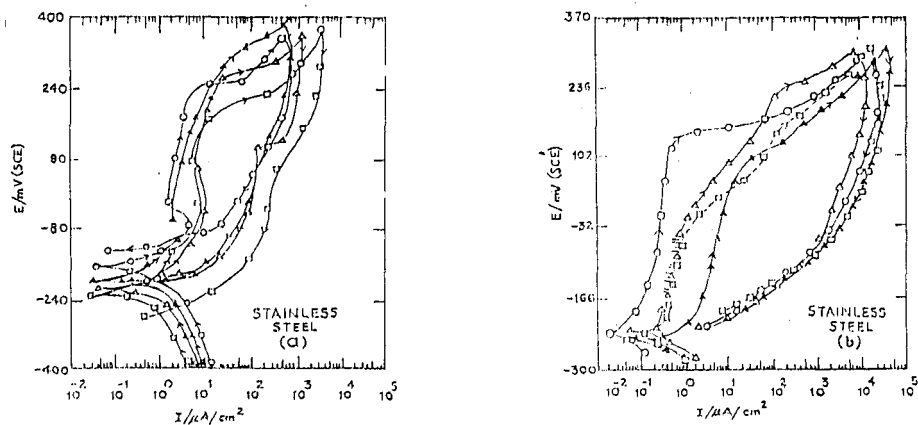


Fig.2a,b :Potentiodynamic anodic polarisation curves at (a) 0 hour and (b) 24 hour for 304 stainless steel exposed to media containing *Commonas testosteronii* (Δ), *Desulphovibrio vulgaris* (\blacktriangle) Coculture (\square), abiotic control (\circ);

Only a few reports have been made dealing with AC impedance studies on stainless steels in presence of biofilms (ref. 15). The AC impedance technique, however, provides surface averaged information on interfacial characteristics and does not help much in precise interpretation of localised pitting processes (ref. 16). In the present work therefore, measurements were carried out during a limited period (24h) of exposure of 304 stainless steel test electrodes. This duration was short so as to initiate any localised corrosion but long enough to bring about biogenic interactions over the test electrode surface. At 0h electrode exposure, Cole-Cole plots exhibited higher frequency arcs of semicircles (Fig. 3a-i). After 24h, these became deformed towards straight line loci at lower frequencies in all the media except that containing *C.testosteronii* (Fig. 3a-ii). A similar behaviour was earlier attributed to the predominance of diffusion control process taking place on both active and passive metals covered with defective polymeric films (ref. 17). *C.testosteronii* tended to increase charge transfer controlled interactions within 24 hrs, the abiotic medium and the mixed culture in particular, continued to show a diffusion controlled response. This is clear from the Randles plots (Figs. 3b-i and ii). Further, the experimental media were heterogenous. They contained various transporting charge carriers, varying concentrations of electrolytic species and precipitated products of the biofilm. All these might create changes in the diffusion characteristics of the interface.

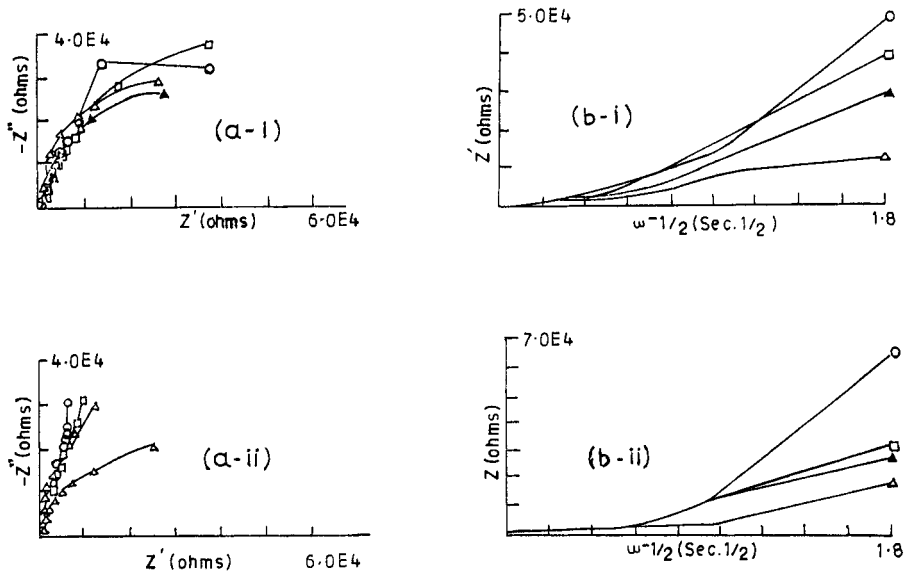


Fig.3a,b AC impedance data: (a) ColeCole plots [(i) 0 hour and (ii) 24 hour]; and(b) Randles plot [(i) 0 hour and (ii) 24 hour] for 304 stainless steel exposed to media containing *Comamonas testosteronii* (Δ), *Desulphovibrio vulgaris* (\blacktriangle); Coculture (\square); abiotic control (o).

In the mixed culture medium, to which 304 stainless steel has been exposed, the dissolved oxygen content in the interfacial region was expected to be low. The rate determining localised corrosion process was therefore dominated by cation diffusion through the defective surface film containing corrosive products and biogenic sulphides. It has been reported that iron sulphide is cathodic to steel (ref. 18) and that biogenic sulphides contribute to the passive effect (ref. 19). Such passivity of the film formed in the presence of a mixed culture, however, becomes fragile under the fluctuating electrical field. The break-down of the temporary passivity of the film gets accelerated by acidic metabolites of the bacteria (ref. 20), such as formic and valeric acids, and hydrogen sulphide produced by *C.testosteronii* and *D.vulgaris* respectively. Formic acid is known to be a relatively strong reducing agent as well as a proven corrosive species particularly in the presence of chlorides. It is likely that under the reducing conditions created by biogenic formic acid, valeric acid, hydrogen sulphide and chlorides, the surface film of 304 stainless steel would be deteriorated in varying degrees depending upon the extent of the prevailing concentrations of the chemical species. All these conditions on 304 stainless steel surface contribute to rapid initiation of biocorrosion.

Biofilms mediate the interactions between surfaces and environment resulting in microbiologically influenced corrosion failures. The present work, related to biocorrosion of structural materials like mild steel, 304 stainless steel and copper in presence of aerobic and anaerobic bacteria, as well as future research will increase our ability to understand metal-microbe interactions and interfacial properties of metallic surfaces covered with biofilms. This in turn will help in characterizing metal-biofilm systems, providing details of biocorrosion mechanisms and quantifying impact of microbes on materials performance.

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